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GROSSULAR FROM METAMORPHOSED DEVONIAN CARBONATE ROCKS OF THE DĘBNIK ANTICLINE (S POLAND)

Abstact. The late Paleozoic rhyodacite intrusion resulted in a 300 m thick contact aureole in the Devonian country rocks of the Dębnik anticline. Contact metamorphism of dolomites led to the formation of calcite-brucite marbles. The metamorphism of dolomitic marls caused the formation of calc-silicate rocks composed mainly of serpentines and calcite. A detailed study of the calc-silicate rocks from the Dubie quarry revealed the presence of indistinguishable in hand specimens, small (50–100 μm), isometric crystals. The crystal habit (rhombic dodecahedron), optical properties, XRD, IR, and SEM-EDS data allowed the identification of grossular. The occurrence of grossular is a characteristic feature of thermally metamorphosed impure carbonate rocks infiltrated by H_2O-rich externally buffered fluid.

Key-words: grossular, contact metamorphism, dolomites, Dębnik anticline

INTRODUCTION

Studies of contact metamorphism of the Dębnik anticline can be traced back to the end of the 19th century, when Szajnocha (1890) encountered the thermal contacts of Carboniferous limestone adjacent to 2 m thick dyke of volcanic rock in the Szklary village (Fig. 1, outcrop III). In the contact zone black limestones were altered to white or grey marble. Apart from calcite, this marble was composed of hematite, kaolinite, wollastonite, epidote, tremolite, and rare grossular (Siemiradzki 1890). Since subsequent research did not confirm this mineral assemblage (Rozen 1909), a new hypothesis was proposed. The mineral paragenesis was presumed to be brought to the surface by intruding volcanic rock as a ksenolith (Gaweł 1953; Kozłowski 1955).

Boreholes situated on the anticline revealed the porphyritic laccolith in its centre, and a broad contact aureole in Devonian country rocks (Narkiewicz 1983). These thermally metamorphosed rocks crop out in the Dubie quarry (Fig. 1, outcrop I), and in nearby Dębnik (Fig. 1, outcrop II). The most common metamorphic rock is

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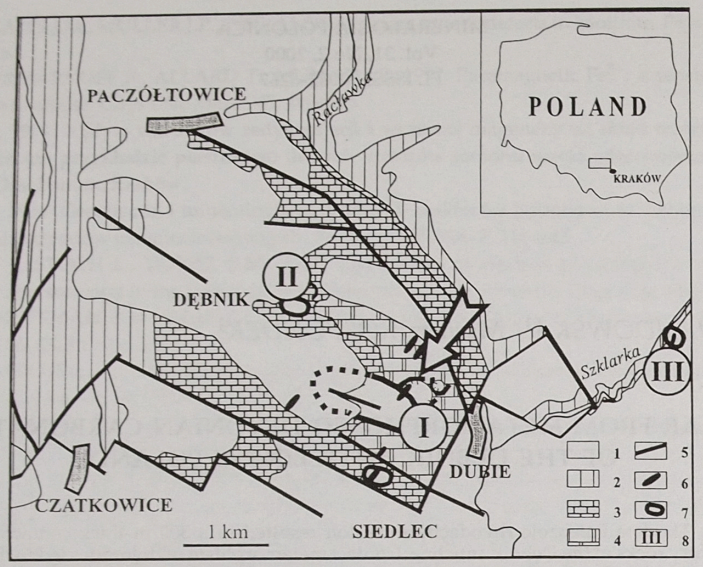

Fig. 1. Geologic map of the Dębnik anticline [according to Kozłowski (1955) and Łaptaś (1982), modified]
1 — Jurassic limestones and sandstones, 2 — Carboniferous limestones, 3 — Devonian limestones, 4 — Devonian dolomites, 5 — faults, 6 — volcanic rocks, 7 — alteration zones, 8 — outcrops

calcite-brucite marble with subordinate dolomite. Other minerals described from metamorphosed rocks of the contact aureole in the Dubie area are: Mg-serpentines, spinel, sepiolite, hydrotalcite, quartz, chalcedony, barite, adularia, smectite, chlorite, kaolinite, periclase, andradite, pyroxenes, forsterite, with minor Fe, Zn and Pb oxides and sulphides (Buczek 1965; Kubisz, Buczek-Półka 1972; Harańczyk, Wala 1989; Harańczyk, Lewandowska 1994; Lewandowska 1989, 1991, 1996, 1997a, 1997b, 1998; Muszyński, Wyszomirski 1998).

Current investigations of the calc-silicate metamorphic rocks have supplied new data, and this paper is devoted to the identification of a newly found mineral — grossular.

MATERIALS

Samples were collected in the Dubie quarry (Fig. 1, outcrop I), situated at the northern margin of the zone of strongest alterations, caused by the 3 km large rhyodacite laccolith (Kurbiel 1978; Muszyński, Pieczka 1994). The metamorphosed rocks are accessible in the southern part of the quarry. Samples were collected at the bottom of the third quarry level (altitude 340 m), between 1988 and 1999 as the successive exploitation went forward.

METHODS

All samples were analysed by powder X-ray diffractometry (XRD) using a horizontal goniometer (HZG-4B), Cu-Kα radiation and Ni-filter. The observation of crystals' habit were performed with a JEOL 5410 scanning electron microscope (SEM) coupled with an energy dispersive spectrometer EDS (EDAX V-9800) for analysis of major-element content. Infrared absorption spectra (IR) were obtained at ambient temperatures with 2.0 cm^{-1} resolution, for a range of 400–4000 cm^{-1}, using a BIO-RAD Fourier Transform Spectrometer (FTS 135) equipped with a Michelson interferometer. The samples were vacuum-pressed into KBr discs.

For a detailed examination, one sample (DUO-12) was crushed, treated with acetate buffer (pH = 5.6) and washed. This procedure was continued until all carbonates were removed. Heavy minerals from the residue (sample DUO-12-2) were separated using bromoform (ρ =2.89 g/cm^3), and studied with XRD, IR and SEM-EDS techniques.

RESULTS

The most common metamorphic rock is predazzite (calcite-brucite marble) formed at the expense of dolomite layers. Among the dolomites, horizons of dolomitic-marly breccia occurred, whose alterations led to the formation of calc-silicate rocks, which are the subject of this investigation. The metamorphosed breccia consists of angular grey carbonate clasts of variable sizes (from 1 to 5 cm) with brown outer zones built of silicates (e.g. sample DUO-12, Phot. 1). The breccia matrix is greenish, sometimes yellowish, very fine-crystalline. The whole rock is intensely serpentinized. Brown, green and white serpentines (Lewandowska 1998) occur mainly in the matrix, but also penetrate the carbonate fragments, generating a "pseudo-agate" zonation. The XRD investigation showed that the mineral composition of the altered calc-silicate rock includes calcite and serpentine with traces of dolomite (sample DUO-12, Fig. 2A). Additionally, small, colourless, isometric, high relief garnet crystals were found in the calcite-serpentine fine-crystalline matrix (Phot. 2). They are grouped in irregular lenses of a width of 1 mm to several centimetres. These crystals were observed in six samples (DU-253, DUO-12, DUO-10, DU-3, DU-256, DU-41). Their size ranges from 50 to 100 μm (sporadically 200 μm). Under crossed polars they show weak birefringence, and sometimes sector extinction.

Heavy liquid treatment have allowed separation of these euhedral crystals, which constitute up to 3 wt.% of the sample (DUO-12). The separated crystals are hardly visible in methylene iodide, that indicates their refractive index n = 1.74. The crystals are developed as rhombic dodecahedra (Phot. 3). The garnet composition (EDS analyses, Fig. 3 and Table 2) is very close to the grossular end-member with small substitution of andradite and almandine molecules. This identification was confirmed by XRD analysis (sample DUO-12-2, Fig. 2B). When compared with the data of pure grossular, the $d_{(hkl)}$ values are slightly shifted towards higher values, characteristic of andradite (Table 1). Additional reflections are characteristic of dolomite and serpentine

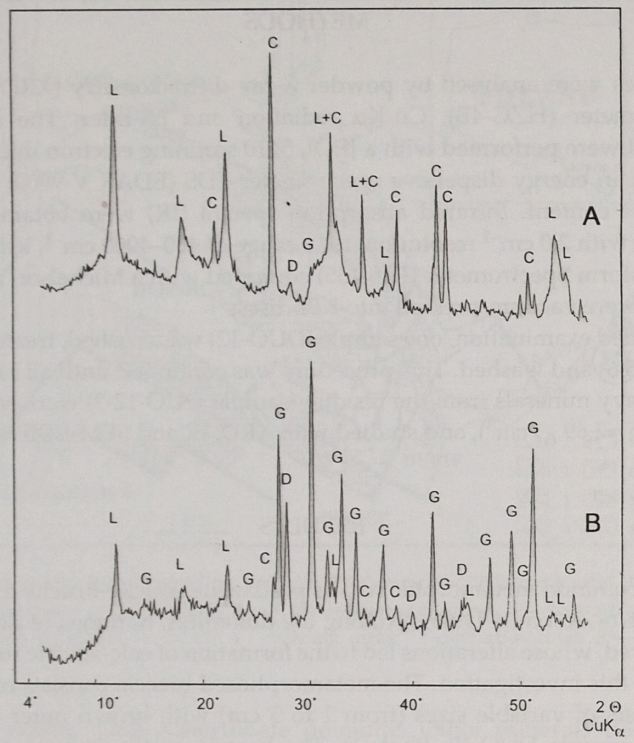

Fig. 2. XRD pattern of an altered calc-silicate rock (DUO-12) and the heavy fraction of this sample after acetate buffer treatment (DUO-12-2) (C-calcite, D-dolomite, G-grossular, L-lizardite)

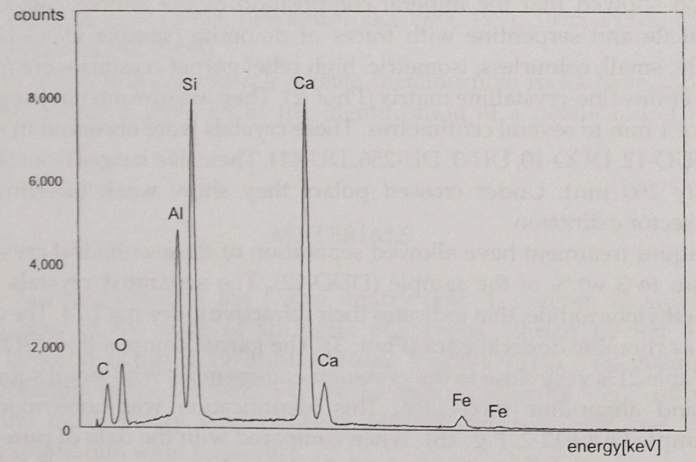

Fig. 3. EDS spectrum of the garnet (sample DUO-12-2)

TABLE 1

XRD-data of grossular from Dubie (sample DUO-12-2) compared to JCPDS data

Grossular from Dubie (DUO-12-2)		Grossular 33-260*		Andradite 10-288*		Other phases
d_{hkl} [Å]	I [%]	d_{hkl} [Å]	I [%]	d_{hkl} [Å]	I [%]	
7.34	30					L
4.85	5	4.831	9			
4.60	10					L
nv	0	4.184	9	4.255	12	
3.658	18					L
3.176	5	3.165	6			
3.037	17					C
2.974	70	2.959	55	3.012	60	
2.892	45					D
2.658	100	2.646	100	2.695	100	
nv	0			2.571	12	
2.530	30	2.525	5			
2.500	18					L
2.426	55	2.415	35	2.463	45	
2.334	45	2.326	15	2.364	15	
2.284	5					C
2.169	30	2.165	20	2.203	15	
2.098	3					C
2.016	2					D
1.930	30	1.923	30	1.957	25	L
1.876	10	1.873	9	1.908	12	
1.805	8					D
1.792	6					D + L
1.716	25	1.709	8	1.739	10	
1.649	38	1.642	20	1.672	25	
1.611	5	1.613	4	1.642	4	
1.589	70	1.582	55	1.610	60	
1.535	5					L
1.507	4					L
1.484	10	1.481	10	1.508	1	

* JCPDS data.
L — lizardite, C — calcite, D — dolomite; nv — not visible.

TABLE 2

The chemical composition of garnet based on EDS analyses

Component	Analysis no.						
	1	2	3	4	5	6	mean
SiO_2	39.58	40.29	40.29	39.82	39.24	38.97	39.70
Al_2O_3	21.04	22.23	22.01	22.18	18.63	17.28	20.56
Fe_2O_3	3.25	1.92	2.00	2.10	3.37	5.72	3.06
TiO_2	0.28	0.00	0.00	0.00	0.47	0.44	0.20
CaO	35.85	35.56	35.69	35.90	38.29	37.59	36.48
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Number of ions on the basis of 12O							
Si	3.00	3.01	3.02	2.99	3.00	3.00	3.00
Al	1.88	1.97	1.94	1.97	1.68	1.57	1.84
Fe	0.12	0.11	0.11	0.12	0.19	0.33	0.17
Ti	0.01	0.00	0.00	0.00	0.03	0.02	0.01
Ca	2.93	2.86	2.87	2.89	3.14	3.10	2.97
Total	7.94	7.95	7.95	7.97	8.04	8.02	7.98

(lizardite), which not dissolved completely in acetate buffer, and occur in traces. These minerals can intergrow the grossular crystals, and thus were not removed in the process of separation. The unit-cell parameter of this garnet is 11,89 (±0,02) Å. This value has excluded the presence of a hydrogarnet, as the lattice parameters of hydrogrossular is usually much higher than 11.85 Å, reaching in most cases *ca* 12.00 Å (Żabiński 1966).

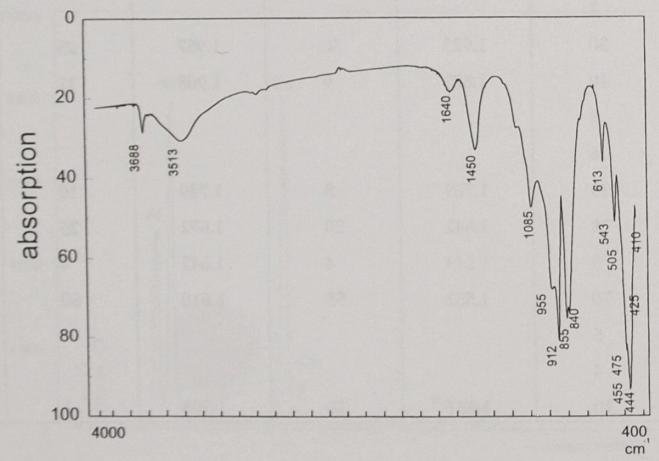

Fig. 4. Infrared absorption spectrum of the garnet (sample DUO-12-2)

TABLE 3

Infrared absorption data (sample DUO-12-2)

Garnet DUO-12-2	Grossular*	Andradite*	Other phases*
cm^{-1}			
410			
425		438	
444			serpentine
455	450		
475	470	482	
505		512	
543	540		
613	618	592	serpentine
840	840	820	
855	860	840	
912	915	895	
955	960	930	serpentine
1 085	1 080	1 185	serpentine
1 450			carbonates
1 640			serpentine + H_2O
3 513			serpentine + H_2O
3 688			serpentine

* According to Moenke (1966).

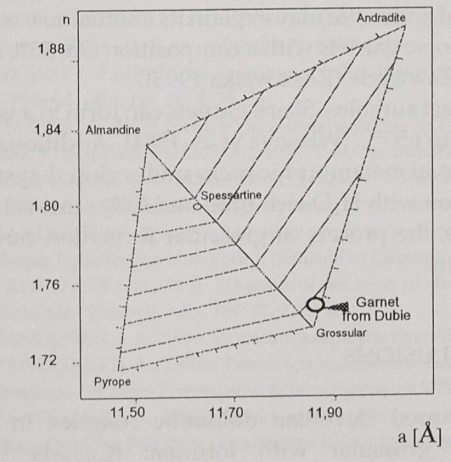

Fig. 5. The correlation among the unit-cell parameter and refractive index within the garnet group (Winchell 1958), with the position of garnets from Dubie

Infrared absorption spectrum is shown in figure 4. The main absorption bands correspond well with those noted for grossular in the literature (Table 3, Bell et al. 1995; Allen, Buseck 1988). The additional bands in the range 3500–3700 cm^{-1} and the band 1085 cm^{-1} may be attributed to serpentine, and furthermore that of 1450 cm^{-1} to carbonates (Moenke 1966).

DISCUSSION

This study has resulted in the detection of garnet in thermally altered Devonian rocks in the Dubie quarry. The garnet identified is near the end-member grossular with the average formula based on EDS data $(Ca_{2.97}Fe^{+2}_{0.04})(Al_{1.84}Fe^{+3}_{0.13}Ti_{0.01})[Si_{3.00}O_{12}]$.

This formula corresponds to garnet composed in 93% of grossular ($Ca_3Al_2Si_3O_{12}$), 6% of andradite ($Ca_3Fe_2Si_3O_{12}$) and 1% of almandine ($Fe_3Al_2Si_3O_{12}$) molecules.

It is generally accepted that the length of the cell edge is an additive function of the molecular proportions of the end members within the garnet group (Winchell 1958). The calculated unit-cell parameters of the garnet from Dubie (a = 11.89 Å) and measured refractive index (n = 1.74) confirmed the identification of grossular (Fig. 5). The habit of the mineral studied, i.e. rhombic dodecahedron (Phot. 3), is an additional evidence of a high content of grossular molecule (Fig. 6, Kostov 1968 *vide* Deer et al. 1992).

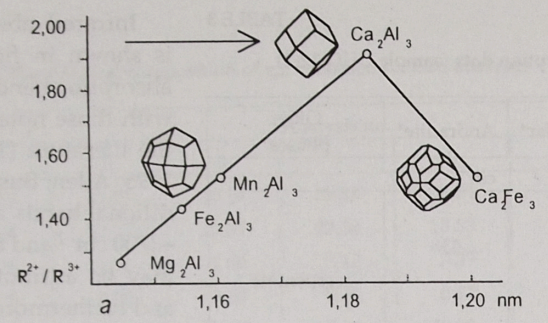

Fig. 6. Variation of habit of garnet crystals in relation to the cation ratio (R^{2+}/R^{3+}) and unit-cell parameter (*a*) (Kostov 1968 *vide* Deer et al. 1992). The arrow indicates rhombic dodecahedron characteristic of garnet crystals from Dubie

The grossular from Dubie exhibits anomalous anisotropy. Optical birefringence is common in calcic garnets, especially those associated with contact metasomatic, and hydrothermal ore deposits (Allen, Buseck 1988). The existence of non-cubic garnet, and garnet-like structures was described by many authors (Aubry et al. 1969; Prewitt, Sleight 1968; Janeczek 1997). Degree of ordering of Al^{+3} and Fe^{+3} in octahedral positions was proposed to explain this feature. The strain induced in the crystal results in the lattice mismatch, thereby reducing the cubic symmetry (Takeuchi et al. 1982; Allen, Buseck 1988). The experiments of Kalinin (1967) proved the correlation of birefringence with chemical composition. Pure grossular and andradite were isotropic but the admixture of several percent of andradite (Adr) to grossular (Grs) caused anisotropy. The highest birefringence show garnets with the Grs-50% and Adr-50% content. In the grossular from Dubie, the 6%-admixture of andradite may explain its anomalous, weak birefringence. In the adjacent area, anisotropic garnets with a composition Grs 50% and Adr 50% were described from a skarn in Zawiercie (Koszowska 1995).

Grossular is a common mineral in contact aureoles. Skarn garnets can form in a wide temperature range estimated for 350° up to 650°C (Własova et al. 1984). Additionally, grossular is a mineral which does not form in metamorphic rocks under closed-system conditions, since it requires rock interaction with H_2O-rich fluid and CO_2 removal (an open system) (Bucher, Frey 1994). Hence, the process of grossular formation cannot indicate the temperature of metamorphism.

CONCLUSIONS

The garnet found in the metamorphosed Devonian dolomitic complex in the Dubie quarry is nearly end-member grossular with formula: $(Ca_{2.97}Fe^{+2}_{0.04})(Al_{1.84}Fe^{+3}_{0.13}Ti_{0.01})[Si_{3.00}O_{12}]$. Its formation is limited to maximally 3 m thick layers developed at the expense of dolomitic-marly breccias. The richest in grossular rocks contain about 3 wt.% of this garnet. Grossular cannot be used as an indicator of metamorphism temperatures, since this mineral can form in a wide range of temperatures in an open system environment.

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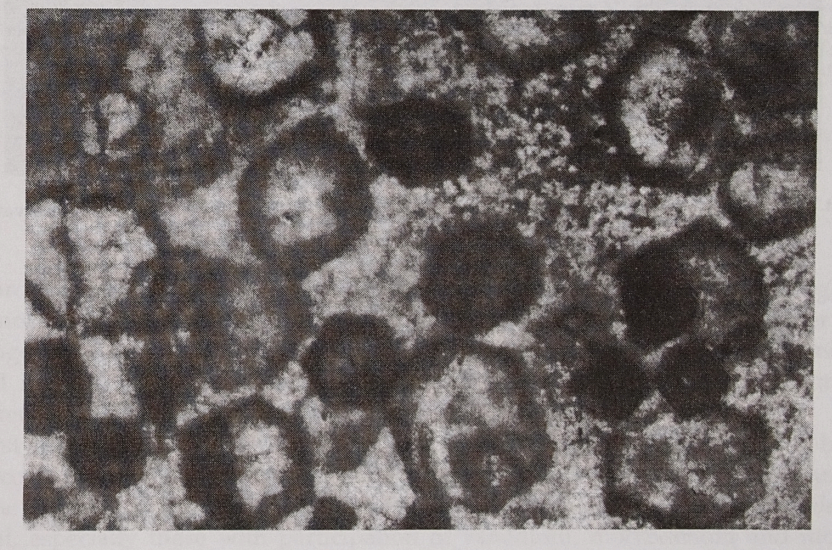
GROSSULAR ZE ZMETAMORFIZOWANYCH SKAŁ WĘGLANOWYCH ANTYKLINY DĘBNIKA

Streszczenie

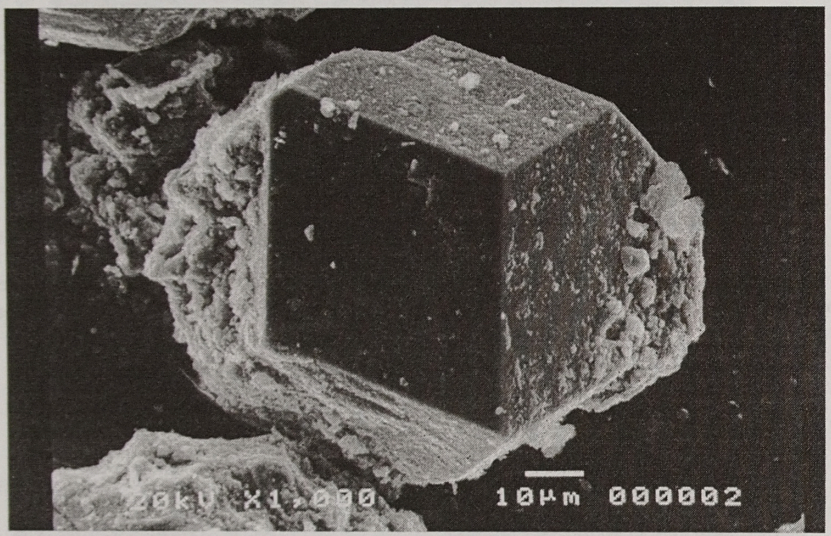
Późnopaleozoiczna intruzja ryodacytowa spowodawała powstanie aureoli kontaktowej w otaczających dewońskich dolomitach i marglach dolomitycznych. Metamorfizm termiczny dolomitów doprowadził do utworzenia marmurów kalcytowo-brucytowych (predazzytów). Metamorfizm margli dolomitycznych spowodował powstanie skał wapienno-krzemianowych zbudowanych głównie z kalcytu i minerałów grupy serpentynu. Szczegółowe badania tych wapienno-krzemianowych skał, z kamieniołomu w Dubiu, pozwoliły ponadto na stwierdzenie obecności małych (50–100 μm), regularnych kryształów granatów. Pokrój (dwunastościany rombowe), własności optyczne, dane XRD, IR oraz SEM-EDS umożliwiły identyfikację grossularu. Obecność grossularu jest cechą charakterystyczną zmetamorfizowanych kontaktowo skał węglanowo-marglistych, infiltrowanych, w systemie otwartym, przez fluidy hydrotermalne.

Phot. 1. Metamorphosed calc-silicates: angular fragments of grey carbonates of variable size (from 1 to 5 cm) with brown outer zones of silicates. The matrix where grossular is present is greenish, sometimes yellowish, very fine-crystalline



Phot. 2. Grossular in plane-polarized light. Small (50 to 100 μm), colourless, high relief crystals are garnets

A. LEWANDOWSKA, M. ROSPONDEK — Grossular from metamorphosed Devonian carbonate rocks of the Dębnik anticline (S Poland)



Phot. 3. Rhombic dodecahedron of grossular from Dubie in scanning electron microscope observations